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(72) Schuster, Georg, DE

(72) Kastle, Hans, DE

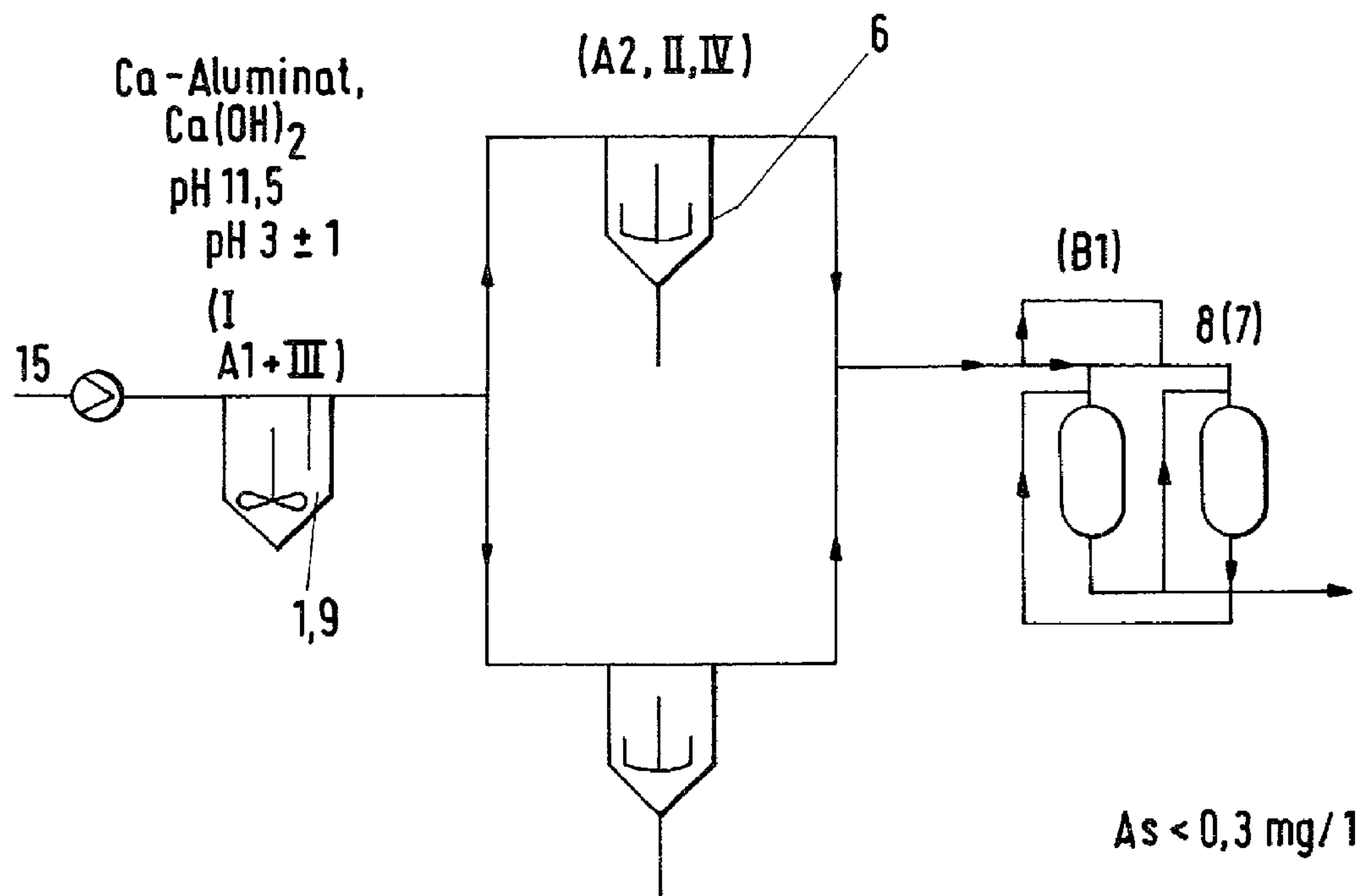
(73) Walhalla-kalk Entwicklungs- und Vertriebsgesellschaft mbH, DE

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(54) **METHODE ET APPAREIL POUR SEPARER L'ARSENIC DES  
DECHETS**

(54) **PROCEDURE AND APPARATUS FOR SEPARATING ARSENIC  
FROM WASTE MATERIAL**



(57) The invention involves a process as well as apparatus for the separation of arsenic from waste material. The process includes precipitation of arsenic in the form of low solubility calcium magnesium arsenates by adding calcium and magnesium compounds to the waste, separation of calcium magnesium arsenates, putting the waste in contact with an ion exchanger, regenerating the ion exchanger after reaching the charge limit, adsorptively separating the arsenic by putting the waste in contact with active carbon, and separating the charged active carbon by itself or along with precipitation products. The process allows for a separation of arsenic from waste which is hard to be treated or contains heavy metals such as lead or contains sulfates to residual amounts as low as <0.3 mg As/l.

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ABSTRACT OF THE INVENTION

The invention involves a process as well as apparatus for the separation of arsenic from waste material. The process includes precipitation of arsenic in the form of low solubility calcium magnesium arsenates by adding calcium and magnesium compounds to the waste, separation of calcium magnesium arsenates, putting the waste in contact with an ion exchanger, regenerating the ion exchanger after reaching the charge limit, adsorptively separating the arsenic by putting the waste in contact with active carbon, and separating the charged active carbon by itself or along with precipitation products. The process allows for a separation of arsenic from waste which is hard to be treated or contains heavy metals such as lead or contains sulfates to residual amounts as low as  $<0.3$  mg As/l.

PROCEDURE AND APPARATUS FOR SEPARATING  
ARSENIC FROM WASTE MATERIAL

FIELD OF THE INVENTION

The invention involves a highly effective procedure as well as apparatus for separating arsenic from waste material, particularly industrial waste.

BACKGROUND OF THE INVENTION

A large number of industrial processes cause low to high levels of arsenic in effluents, which cannot effectively be separated during waste purification processes with present technology.

In the production of lead crystal and crystal, arsenic trioxide ( $\text{As}_2\text{O}_3$ ) is added, up to an amount of 2 mass-% of the molten glass, as a purifying agent. Annually, 400 metric tons of arsenic are used for this purpose in the Federal Republic of Germany. Due to present technical limitations, the arsenic cannot simply be substituted with another, safer purifying agent. While part of the used arsenic escapes from the molten glass, an amount of approximately 0.2 mass-% remains in the combined state found in the glass matrix.

However, during refining processes in which the surface is worked on, arsenic is again released. This happens in the so-called acidic polishing process, during which the glass is treated with sulfuric acid - hydrofluoric acid mixtures and the glass partially dissolves again, as well as during the process of cutting glass. Acidic polishing baths contain approximately 40 - 100 mg As/l while waste from cutting procedures contains typically approximately 1 mg As/l or when recirculated up to approximately 10 mg As/l.

Furthermore, arsenic containing lyes occurs when producing nonferrous metals. This water soluble arsenic is found in soda slag of pyrometallurgical processes with a concentration up to 400 mg As/l. Solutions with relatively high concentrations, around several mg/l of arsenic, also occur during wet waste gas purification, such as the desulfurization of flue gas, and in eluates of combustion residues. Waste material containing arsenic also results from the production of micro chips when etching the gallium arsenide used therefor.

Due to the high toxicity of arsenic there is a great need to diminish the content of arsenic in waste material as much as possible.

Surveys regarding the removal of arsenic from effluents produced by the glass industry when cutting glass are described in the research article 10207001/06, dated August 1986, produced by the Fraunhofer-Institute for Silicate Research in Wurzburg, Federal Republic of Germany. This research was conducted within the Plan for Environmental Research by the Federal Minister for Domestic Affairs of the Federal Republic of Germany. Industrial effluents such as these contain up to approximately 3 mg As/l and up to approximately 10 mg Pb/l as well as cooling agents, lubricating agents and tenside. The pH-value of such effluents is between 7 and 8.

Within the scope of these surveys several different procedure possibilities for separating arsenic from waste have been tested systematically. Aside from experiments of reducing arsenic on the surface of metals, such as iron and zinc, other experiments were also conducted to precipitate arsenic as sulfide of arsenic, as calcium arsenate, as ferro arsenate, as magnesium arsenate, as aluminum arsenate, and as arsenate of lead. In all of those cases only a separation degree of less than 50% could be obtained.

Further experiments examined separation by means of adsorption to silica gel containing titanium oxide, alumina and active carbon. The above research article at page 14

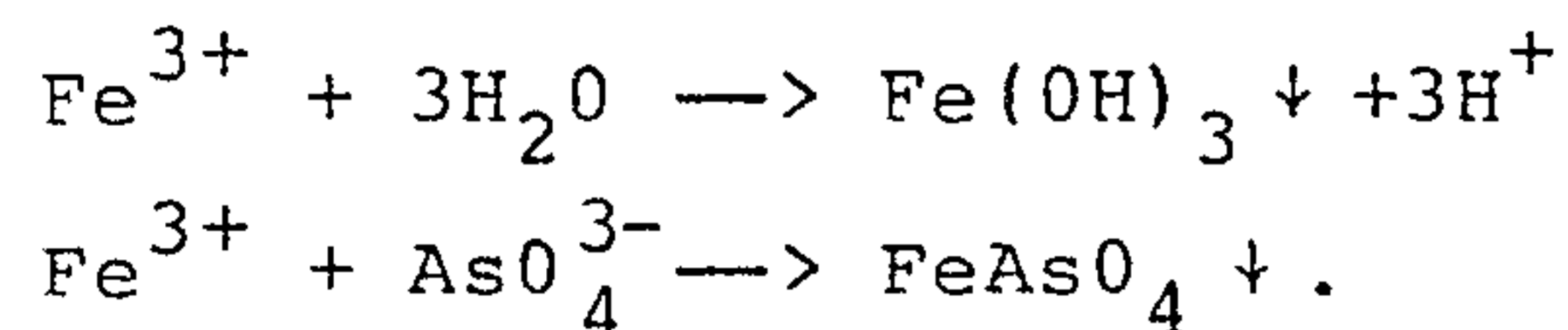
states that no nominal decrease of the arsenic content in waste was noticeable when using silica gel and active carbon. Only the use of aluminum oxide resulted in a minimal decrease of the arsenic content. However, this amount is too small for a practical application.

The only somewhat promising separation method of arsenic among all the systematically conducted experiments turned out to be the precipitation with ferric salts with or without previous oxidation of As(III) to As(V). This procedure resulted in a decrease of arsenic from 4 mg/l to less than 0.1 mg/l in suitable effluents. In waste material produced by acidic polishing in the glass industry, which can contain arsenic up to 100 mg/l in strongly acidic solutions, the content of arsenic could only be reduced by one half through precipitation of sulfide of arsenic, through the resolution of iron sulfide in acidic waste (see page 50 of the research article).

In other words, samples with an initial content of arsenic of approximately 15 mg/l subsequently still contained 6 to 7 mg/l of arsenic. Due to the extensive amount of experiments regarding the separation of arsenic (see page 50 of the research article) it is thus established that according to current technology even an elaboration of a proposal of a possible technical procedure

for separating arsenic requires further laboratory experiments. The research article, on page 51, points out that there is no existing proposal for a procedure that will separate arsenic from effluents produced by acidic polishing.

In the publication "Ecologically Harmless Technologies For The Production Of Lead Crystal And Crystal - Removal Of Arsenic From Effluents Produced When Cutting Glass" of the Fraunhofer Institute for Silicate Research, Wurzburg, Federal Republic of Germany, the separation of arsenic from waste is described as a formation of ferro arsenate under coprecipitation in a ferric hydroxide precipitation which occurs according to the following gross reaction equation:



To avoid a decrease of the pH-value due to the added iron sulfate, a calcium hydroxide suspension is used for neutralization, whereby the sulfate ions are precipitated as gypsum. This procedure allows, however, only for waste with small amounts of arsenic, for a reduction of the arsenic content up to an amount below 0.1 mg/l, but this is not applicable to effluents from acidic polishing

procedures. In this case only 50% of the arsenic content can be separated.

The article ATV-VKS M352 (dated April 1987) on the "Treatment and Removal of Scorodite Mud" suggests to transform water soluble arsenic from pyrometallurgic procedures (scorodite = ferrous arsenate  $\text{FeAsO}_4$ ) in a concentration of 1000 to 4000 mg/l in a sulfuric solution into arsenic(V) with the aid of chlorine and to precipitate it at temperatures of 60 to 70°C and pH-values of less than 1 by means of adding ferric salts and subsequent careful raising of the pH-value to 2 to 2.5 with calcium hydrate. The article did not give any remarks on the efficiency of the precipitation or the remaining concentration of dissolved arsenic. In some processes, 0.3 to 2 mg As/l, 50 to 300 mg Cu/l, 100 to 300 mg Zn/l, 1 to 3 mg Pb/l, 0.1 to 1 mg Fe/l as well as 500 mg Cl/l have been found in the eluates. The amounts of sulfate and calcium correspond approximately to the solubility of plaster. This publication also points out that no alkaline reactions and no reduction procedures should be carried out in order to not increase the solubility of arsenic.

The separation of arsenic from waste according to the above described procedure, the precipitation as ferro arsenate, is further also the subject of Germany patent

publications 3,632,138 and 3,633,066, with or without previous oxidation of the trivalent arsenic.

The separation of arsenic from waste by means of precipitation of ferro arsenate is thus only applicable to certain, suitable effluents and is not a generally suitable separation procedure for arsenic.

German patent publication 3,637,643 further describes a procedure for the arsenic decontamination of aqueous solutions, which is based on the oxidation of arsenic(III) to arsenic(V) and the pressure filtration of waste after adding a water soluble polymeric anion exchanger through a membrane.

According to this method the anion exchangers are polymers with molar masses of 30,000 to 100,000 in connection with membranes of a preclusion limit of  $10^4$ , for example, polyethylenimine. The arsenic concentration of the solution to be decontaminated must not be higher than 2 mg/l if this procedure is applied in one step. Due to the method of membrane filtration used here, this procedure is basically not suitable for an application on a technical-industrial scale.

## SUMMARY OF THE INVENTION

It is an important purpose of the invention to provide a procedure as well as an apparatus for a highly efficient separation of arsenic from waste material, which would be applicable to industrial effluents and which would make it possible to reduce the arsenic to corresponding final concentration values conforming with waste regulations regardless of the origin of respective effluents. The procedure ideally starts out with cheap, readily available materials that do not result in further environmental problems. The procedure also operates highly economically with respect to the consumption of energy and material and is as well applicable to waste which is difficult to treat.

The method for separating arsenic from sewage according to the invention is characterized by following steps:

(A1) Precipitation of arsenic in the form of low solubility calcium magnesium arsenate by adding calcium and magnesium compound to the effluents at a pH-value of 2 to 12 and preferably 9 to 11 during a precipitation span of approximately 10 to 60 min., preferably 30 min., and

(A2) separation of calcium magnesium arsenate, and/or

(B1) putting the effluents in contact with an ion exchanger, preferably a strongly basic anion exchanger, at

a pH-value of 2 to 12 and preferably 7 to 11.5, and, if desired

(B2) regenerating the ion exchanger after reaching the charge limit, and/or

(C1) adsorptively separating arsenic through putting it in contact with active carbon at a pH-value of 2 to 11 and preferably 2 to 4, and

(C2) separating charged active carbon by itself or with precipitation products.

At a suitable pH-value in an alkaline range as well as corresponding excess of magnesium compounds, magnesium hydroxide is precipitated during step A1 which influences the separation result favorably. A particularly favorable condition for the adsorptive separation of arsenic in step C1 is a pH-value of 3 or 11.

A particularly suitable apparatus according to the invention for conducting the procedure mentioned above is characterized by the following fundamental components, the sequence of which corresponds to the reaction course:

- an oxidation and precipitation reactor for the precipitation of calcium magnesium arsenates, which is connectable through connecting tubes to a reservoir containing an oxidation agent, another reservoir for a

magnesium compound and yet another reservoir for a calcium compound, and features a pH-regulation device, and

- a separation reactor for separating the calcium magnesium arsenates from the residual effluents, and/or

- an adsorption reactor to put the sewage in contact with the active carbon, eventually with a regenerating apparatus, and/or

- an ion exchanger, possibly with a regeneration apparatus.

According to current technology the adsorption agents for the adsorptive separation of arsenic are active carbon, aluminum and aluminum oxide as well as silica gel. These agents, however, are said to be not very efficient. Another possibility is the adsorptive bond of arsenic to freshly precipitated magnesium hydroxide. One gram of freshly precipitated magnesium hydroxide is supposed to be able to adsorptively bind 125 mg of arsenic according to bibliographic references. This adsorption capacity has been used when administering magnesium hydroxide as an antidote for poisoning through arsenic.

As explained above, current technology further suggests that arsenic can be precipitated from aqueous solutions as sulfide of arsenic, calcium arsenate, ferro arsenate, manganese arsenate, arsenate of lead and

magnesium ammonium arsenate. Nevertheless, for the same reasons explained above, these precipitation reactions are also not suitable for technical processing of waste material containing arsenic. An additional factor is that the ferro arsenates, scorodite, simplisit and ferrisimplisit, are decomposed by bases and completely soluble in acids.

As apparent from the following Table 1, there is partially very diverse data found in bibliographical references [such as Gmelin, Manual of Anorganic Chemistry, Part B, 8th Edition, Publishing House Chemie, Weinheim (1956)] regarding the solubility of calcium arsenates.

TABLE 1

## Solubility of calcium arsenates in water

Compound	Solubility (mg/l)
$\text{Ca}_3(\text{AsO}_4)_2 \cdot 10 \text{H}_2\text{O}$	170 (20 °C)
$\text{Ca}_3(\text{AsO}_4)_2 \cdot 2 \text{H}_2\text{O}$	133 (20 °C)
$4 \text{CaO} \cdot \text{As}_2\text{O}_5 \cdot 5 \text{H}_2\text{O}$	150 (17 °C)
$4 \text{CaO} \cdot \text{As}_2\text{O}_5$	120 (17 °C)
$4 \text{CaO} \cdot \text{As}_2\text{O}_5 \cdot \text{H}_2\text{O}$	120
Precipitation from hot solutions	
$\text{As}_2\text{O}_5$	32
$\text{Ca}_3(\text{AsO}_4)_2$	55

$\text{Ca}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$  yields up to 3% water soluble arsenic dioxide. Basic tricalcium arsenate  $\text{Ca}_3(\text{AsO}_4)_2 \cdot \text{Ca}(\text{OH})_2$  has furthermore a very low water solubility.

It is therefore safe to assume that calcium arsenates have a solubility in the range of 60 to 200 mg/l, which corresponds to approximately 20 to 70 mg As/l. Calcium salts are hence not suitable for the precipitation of arsenic from waste. Even through their solubility can be lowered by zinc ions, heavy metal ions as well as fluorides or complex fluorides, no significant decrease in solubility of calcium arsenate can be obtained, regardless of the new set of problems such additions would cause.

Bibliographical references further suggest, however, not in respect with the processing of waste, that calcium ammonium arsenate and magnesium ammonium arsenate have low solubility. For that reason calcium magnesium arsenates have not been considered for the separation of arsenic from waste material.

An advantage when applying the procedure according to the invention is to oxidize the arsenic contained in waste, As(III) to As(V) ( $\text{AsO}_4^{3-}$ ) with suitable oxidation agents, such as  $\text{CaO}_2$ ,  $\text{MgO}_2$ , or  $\text{H}_2\text{O}_2$ , at a pH-value in the

acid or alkaline range. In this case a pH-value in the acid range is preferred as well as the use of  $H_2O_2$  because it is converted to water during oxidation. This oxidation can also be carried out simultaneously with the precipitation of the calcium magnesium arsenates.

If the effluents to be treated contain sulfate ions which have to be separated, that process can be accomplished by means of precipitation of calcium sulfate by adding  $Ca(OH)_2$  to the waste material as process step I and separating the precipitated  $CaSO_4$  in process step II. This reaction should preferably be performed at a pH-value of  $3 \pm 1$  if the precipitation of  $CaSO_4$  is done before step A1, and at a pH-value of  $3 \pm 1$  or 8.0 to 11.0, if the  $CaSO_4$ -precipitation is performed before step B1 or C1 respectively, hence particularly after step A2.

Alternatively or after a preceding sulfate separation by means of precipitation of  $CaSO_4$  as described above, sulfates can also be separated in process step IV from the waste through precipitation of calcium aluminate sulfates (process step III) of low solubility by adding reactive aluminum oxide and/or calcium aluminates, preferably aluminous melting cement. The pH-value during this process is maintained at a constant level of 11.2 to 11.8 by adding  $Ca(OH)_2$ .

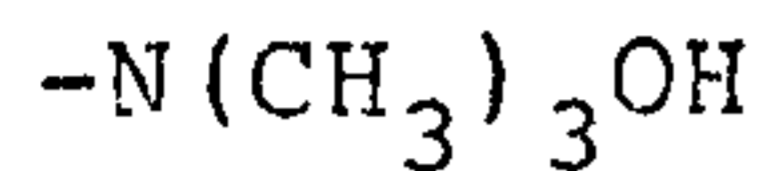
If the preliminary precipitation has been performed with milk of lime at a pH-value of  $3 \pm 1$ , the arsenic contained in the waste remains in solution. This is particularly important since with waste containing large amounts of sulfate as well as concentrated waste, a separation of about 75 to 80% of the entire mud as  $\text{CaSO}_4$  is possible at this level. This mud contains only extraordinarily low amounts of heavy metals and arsenic in particular, so that such mud can be disposed of at customary disposal sites such as construction site disposals. If necessary the arsenic contained in the water of the press cake can be removed by washing at this level. This also applies to the precipitation product of the calcium aluminate sulfate precipitation. This procedure is known from European patent publication 25 06 26.

In a particularly advantageous method of the invention's procedure, which yields an up to now unachieved decrease of the residual concentration of arsenic in the run off water to a value in the range of  $\leq 0.5$  mg As/l, the preliminary treated effluents (preferably from step A2, C2, II or IV respectively) are put into contact with an ion exchanger, preferably a strongly basic anion exchanger, and preferably at a pH-value in the alkaline to neutral range.

Strongly basic anion exchangers are generally interlaced polystyrene resins with a macro-porous structure, which show quaternary ammonium groups as

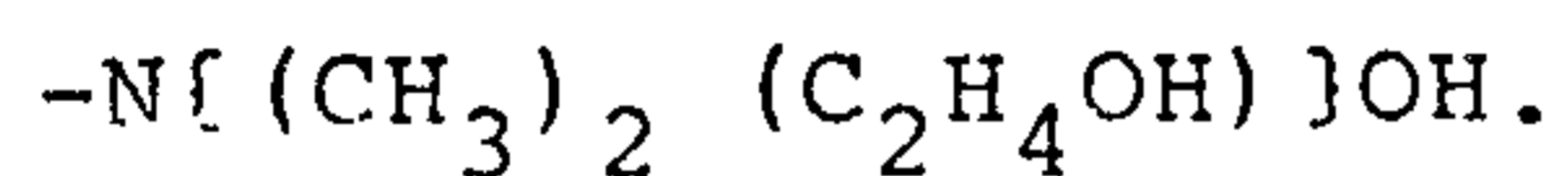
functional groups. With respect to this we have to distinguish between two types:

Type I resins with the active group



and

Type II resins with the active group



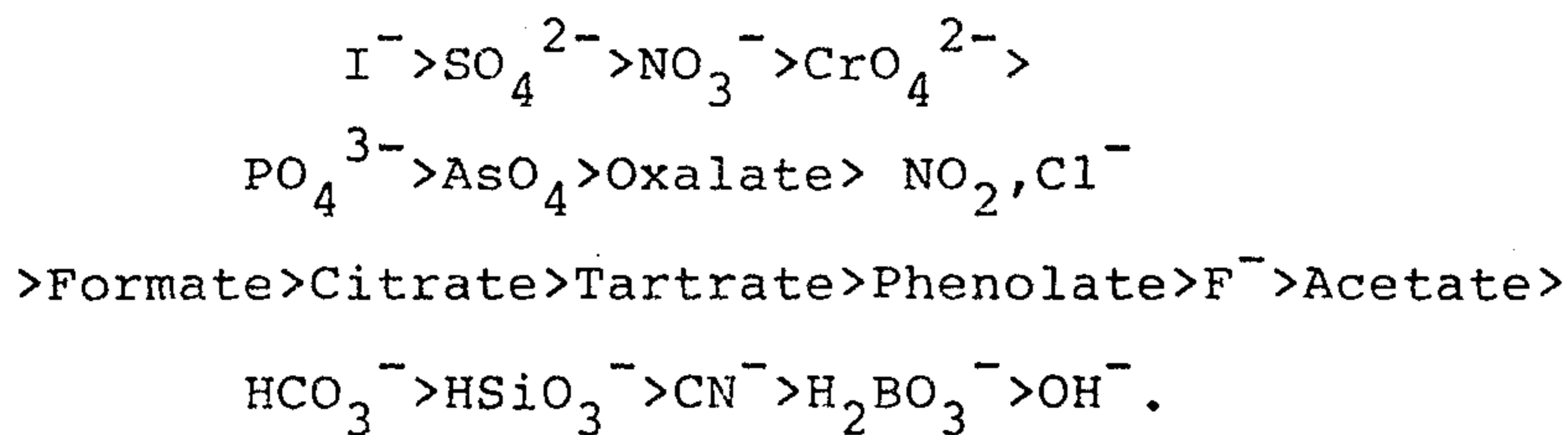
Type I anion exchange resins have a slightly higher basicity with respect to type II anion exchange resins. However, they have a lower capacity and a less distinct regeneration ability, whereas on the other hand, their oxidation susceptibility is lower. Furthermore, type II anion exchangers cause a greater slip.

The most important identifying data of these anion exchangers is:

Total capacity: approximately 1.2 val/l  
moist resin (both types);

Utilizable capacity: 0.4 to 0.6 val/l moist resin  
for type I and approximately  
0.7 val/l moist resin for  
type II.

The affinity of these anion exchangers to various anions accounts for the OH-form of the following sequence:



Macro-porous anion exchanger resins are also suitable for the procedure according to the invention. They even offer additional advantages, insofar that macro-porous anion exchangers have a greater mechanical durability and yield better processing/dressing/treating results and have a greater consistency against poisoning due to water charged with colloids. The charging capacity with organic material is higher for macro-porous exchangers than for conventional resins. Also higher is the elution degree for regeneration.

Furthermore, according to the invention, favorable "mixing bed" ion exchangers can be used, in which cation exchanger and anion exchanger particles occur in one and the same device. In order to obtain regeneration the two resins are separated by hydraulic whirl/swirl measures because the two resins have different densities. After separation the resins are regenerated separately and following regeneration they are transferred into a mixing bed, for example by means of compressed air. Another

advantage is the use of an exchanger cartridge. The regeneration of the ion exchanger resins occurs conventionally, after reaching the charge limit.

Compared with the desalination with separate exchanger beds, the desalination in a mixing bed has the advantage of a very constant quality of water, the use of a pH-value close to the neutral point, as well as a smaller consumption of wash water.

Highly basic anion exchangers require a great NaOH-surplus to transfer into the OH-form. This surplus usually amounts to 200 to 400% of Th., in the form of a 4-5% solution.

According to the invention it is particularly advantageous, when using a mixing bed ion exchanger, to use the anion exchanger in the chloride form and the cation exchanger in the H-form, since regeneration can then occur with hydrochloric acid being the only regenerating agent.

The adsorptive separation of arsenic in the procedure according to the invention occurs by means of putting the waste in contact with active carbon. Different types of active carbon with certain quality differences due to variations normal in production are customary.

The adsorption of arsenic from waste material can occur by entering powderized active carbon into the waste

in step C1 as well as by bringing the effluents in contact with an active-carbon solid bed, which, in effect, is a simultaneous carrying out of steps C1 and C2.

Because of procedural reasons as well as reasons of better regeneration ability, the use of an active-carbon solid bed is preferred in this invention. The regeneration of active carbon takes place in the conventional manner. The thermal regeneration of the charged active carbon conveniently yields the adsorbed arsenic.

The precipitation products or solids from steps A2, C2, II or IV, are washed if necessary, after adjusting the pH-value, with water. In this case the water used for washing is led back into the used crude waste water. Precipitation products and solids from step A2 in particular can be compressed and disposed of. The same applies to steps II and IV. It is also advantageous to return the regeneration solutions from step B2 to step A1, the precipitation of arsenic, or to step C1, the adsorptive separation of arsenic.

Another advantage is to separate the arsenic contained in the regeneration solutions from step B2 in the form of low solubility arsenic compounds, for example, in the form of sulphide of arsenic. In this case the obtained solutions are returned to step A1, the precipitation of

arsenic, or step C1, the adsorptive separation of arsenic. Conveniently they can also be reused as regeneration solutions.

According to the invention calcium and magnesium compounds and specifically adequate salts are used. A favorable calcium compound is calcium hydrate and a favorable magnesium compound is magnesium hydroxide. Alternatively magnesium salts, preferably magnesium chloride, can be used as a magnesium compound in step A1.

The apparatus according to the invention can combine the reservoir for the magnesium compound and the one for the calcium compound, out of which the calcium and the magnesium compounds can be dispensed into the precipitation reactor in a constant, predetermined molar ratio. It can also be an advantage to combine the oxidation and precipitation reactor with the following separation reactor. The eventually provided active-carbon solid bed reactor conveniently contains a regeneration apparatus, which not only regenerates the active carbon but also yields the arsenic it desorbed.

In case the apparatus is used for treating sulphate containing waste, the apparatus of the invention provides a second precipitation reactor which is connectable with the reservoir for milk of lime or calcium aluminate and

contains a pH-adjuster. This second precipitation reactor, which is followed by another separation reactor, serves for the precipitation of calcium sulphate or calcium aluminate sulfates respectively, as described above. This unit, the precipitation reactor followed by the separation reactor, can be placed before the oxidation and precipitation reactor, between the latter and the adsorption reactor or the following ion exchanger.

The separation reactors according to the invention are either sedimentation reactors or centrifuges.

#### BRIEF DESCRIPTION OF THE DRAWING

The objects, advantages and features of the invention will be more readily perceived from the following detailed description, when read in conjunction with the accompanying drawing, in which:

Fig. 1 is a schematic representation of discontinuously functioning apparatus according to the invention for separating arsenic through the exchange of ions with a preliminary separation of sulphate by means of precipitation;

Fig. 2 is a schematic representation of an alternative embodiment of discontinuously functioning apparatus of the

invention to first precipitate and separate calcium magnesium arsenates after preliminary oxidation of arsenic;

Fig. 3 is a schematic representation of apparatus according to the invention for continuous separation of arsenic and processing/treatment of water; and

Fig. 4 is a schematic representation of a more comprehensive continuous treatment apparatus functioning according to the invention.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The individual procedure steps in Figs. 1 to 4, particularly Fig. 4, employ the following identified reference numerals:

- 1 - Oxidation and precipitation reactor
- 2 - Reservoir for oxidation agent
- 3 - Reservoir for calcium compound
- 4 - Reservoir for magnesium compound
- 5 - pH-adjuster
- 6 - Separation reactor for separating precipitated calcium magnesium arsenates
- 7 - Adsorption reactor
- 8 - Ion exchanger
- 9 - Precipitation reactor for the precipitation of sulphate as calcium sulphate or calcium aluminate

- sulphate respectively
- 10- Reservoir for milk of lime
  - 11- Reservoir for calcium aluminate
  - 12- pH-adjuster
  - 13- Thickener
  - 14- Press
  - 15- Waste inlet.

The apparatus of Fig. 1, in addition to providing a preliminary separation of sulphate, also preliminarily separates heavy metals if necessary, by means of precipitation. This apparatus functions discontinuously in the batch production. The concentration of arsenic in the run-off is  $<0.3$  mg/l. The Fig. 2 apparatus first precipitates and separates calcium magnesium arsenates (A1, A2) as well as sulphate and eventually heavy metals, after the preliminary oxidation of As(III) to As(V). This step is followed by another precipitation and separation of sulphate (III, IV) which results in a further reduction of the sulphate content in the remnant waste. After the ion exchanger (B1) there is also a remaining concentration of arsenic of  $<0.3$  mg/l.

The apparatus of Fig. 3 provides for the separation of sulphate as  $\text{CaSO}_4$  in steps I and II, in addition to the continuous separation of arsenic and processing/treatment

of water. Following that is a precipitation of arsenic and heavy metals in steps A1 and A2, which in turn is followed by a further separation of sulphate in the form of calcium aluminate sulphate in the steps III and IV. The final cleaning process again is carried out with an ion exchanger in step B1. Fig. 4 shows another continuous treatment waste apparatus, in the process of which the sulphate (step I, II) and subsequently the major part of arsenic is separated through precipitation as calcium magnesium arsenate (step A1, A2). Following that is another precipitation of sulphate in steps III and IV, which in turn is followed by a final cleaning process in an ion exchanger (step B1). An adsorption reactor 7 can be provided as an alternative to the final cleaning process with an ion exchanger.

Oxidation and precipitation reactor 1 is preferably an agitator vessel in the lower part of which a discharge is arranged which is connected to mud-collecting vessel 13 for the precipitation vessel. Oxidation and precipitation reactor 1 is connected through respective tubes with reservoir 2 for the oxidation agent, reservoir 3 for the calcium compound and reservoir 4 for the magnesium compound (Fig. 4). The reactor also comprises pH-adjuster 5, which

makes pH-control and pH-adjustment possible through adding a suitable reagent from a corresponding reservoir.

Following the oxidation and precipitation reactor is separation reactor 6 where the separation of the precipitated calcium magnesium arsenate from the remnant water occurs. This separation reactor can also be connected with the mud-collecting vessel. The separation reactor is preferably a sedimentation reactor. The arsenic containing mud is commonly separated, dehydrated and disposed of.

Adsorption reactor 7 preferably comprises an active carbon solid bed as well as a regeneration device by means of which the active carbon is regenerated and preferably yields the desorbed arsenic. The adsorption reactor can be a substitution for ion exchanger 8 or it can be an additional device, particularly following step II or step A2. It can also be used instead of oxidation and precipitation reactor 1.

Following the adsorption reactor can be another precipitation reactor 9, basically of the same kind as oxidation and precipitation reactor 1. This reactor would serve for the precipitation of calcium sulfate and/or calcium aluminate sulfates from waste material under adjustment of pH with pH-adjuster 12. For this purpose the

precipitation reactor 9 is preferably connected through supply tubes with reservoir 10 for milk of lime and reservoir 11 for calcium aluminate. Another, unnumbered, separation reactor can follow precipitation reactor 9. In the lower part of this additional reactor is a discharge for the precipitation product which in turn is connected to the mud collecting vessel. Separation reactor 9 is also connected to the collecting vessel.

The separation of at least the remnant arsenic takes place in the ion exchanger, preferably in anionic form. Ion exchanger 8 is preferably an anion exchanger but can also be a mixed-bed ion exchanger. The ion exchanger's regenerative agent can be lead through a regenerative duct back into the process.

The procedure possibilities depicted in Figs. 2, 3, and 4 are provided with a thickener in vessel 13 and a press 14, which may in particular be a chamber filter press for processing mud. Step B2 is the ion exchanger regeneration step, a conventional regeneration process which is not shown in the drawing.

The apparatus according to the invention is controlled by a central control and regulating device which can be provided with a micro computer system. In this case sensors and detectors at corresponding processing stations

control the process. The signals are conveyed to a central unit which in turn operates corresponding regulating units according to a predetermined program. This makes it possible to operate the procedure automatically to a large degree. Particularly important is the control of the recirculation of mud.

The following examples for procedures explain the invention in more detail and refer to comparative experiments. The experiments use very different industrial effluents (Wastes I to IX) as well as two synthetic effluents (Synthetic Wastes I and II). The industrial effluents derive from various acidic polishing processes in the glass industry. They all contained the same substances, the concentration of which however, varied, particularly in those substances which can increase due to recirculation. Previous experiments showed that those effluents, containing high amounts of alkali, particularly Na and K, are very hard to treat. Therefore effluents have been chosen which are of low, medium or high difficulty to be treated.

The composition of the 'crude waste water used before each treatment is given in Table 2.

TABLE 2

Type of Waste	As (mg/l)	Pb (mg/l)	Na (mg/l)	K (mg/l)	F (mg/l)	Add. of Tenside ml/l	Rating
Waste I	12.03	8.00	63.5	139.4	-	-	Easily treated
Waste II	17.01	5.60	109.6	219	-	-	Easily treated
Waste III	24.30	5.00	1063	325	-	-	Hard to treat
Waste IV	28.5	-	318	246	-	-	Medium treatment
Waste V	33.5	-	181	884	-	-	Hard to treat
Waste VI	6.9	11.5	70	120	-	-	Easily treated
Waste VII	14.0	6.2	93	180	-	-	Medium treatment
Waste VIII	10.6	-	397	448	-	-	Hard to treat
Waste IX	22.4	-	769	589	-	-	Hard to treat
Synthetic Waste I	163.3	-	>1000	>1000	>1000*	1	Easily treated
Synthetic Waste II	15.7	-	>1000	>1000	>1000**	1	Easily treated

\* used as  $F^{\theta}$ ,

\*\* used as  $H_2SiF_6$

- means not determined or no additions respectively

Within the framework of the survey it has been attempted to separate As(III) or As(V) respectively from the solutions by means of different precipitation reactions or adsorption respectively, or by means of exchange of ions. The determination of As was generally carried out with atomic adsorption spectrometry (graphite tube technique Ni/As; 1 to 5% analysis error, depending on concentration). By adding  $F^{\ominus}$  and  $H_2SiF_6$  an eventual disadvantageous effect of complex bound arsenic is examined. However, a disruption of the precipitation reactions or the As-adsorption respectively could not be observed. Furthermore it was determined, by adding tensides, whether such agents which lower the interfacial tension disturb the precipitation of calcium magnesium arsenates. Again, no negative effect of such agents could be found.

#### Comparative Example 1

Arsenic has been precipitated with calcium hydrate from various effluents, at room temperature and at a pH-value of 10.5 to 11. Table 3 is a summary of the results obtained. The residual arsenic content is given in addition to the concentration in the percentage of initial arsenic amount (100%) in the used crude waste water. The

degree of arsenic separation corresponds to the percentage of separated arsenic with respect to the initial amount of As in the crude waste water.

TABLE 3

Type of Waste	As (mg/l)	Final As (%)	As separation (%)	Pb (mg/l)	Na (mg/l)	K (mg/l)
Waste I	2.35	19.5	80.5	<0.1	10.2	115.2
Waste II	3.5	20.6	79.4	<0.1	27.6	118.3
Waste III	15.0	61.7	38.3	-	919	274
Waste IV	12.9	45.3	54.7	-	264	246
Waste V	23.9	71.3	28.7	-	159	837
Waste VI	3.0	43.5	56.5	-	70	120
Synthetic Waste I	2.0	1.2	98.8	-	>1000	>1000
Synthetic Waste II	0.2	1.3	98.7	-	>1000	>1000

## Comparative Example 2

This experiment has been conducted with waste VI as shown in Table 3 (As-content 6.9 mg/l, refer to Table 4) and the arsenic has also been precipitated with  $\text{Ca(OH)}_2$ , however without oxidation (Experiments A), or with alkaline oxidation (Experiments B), or with acidic oxidation of

As(III) to As(V) (Experiments C). The pH-value during the  $\text{Ca(OH)}_2$  precipitation was 9.0; the precipitation lasted 45 min. at  $25^\circ\text{C}$ .  $\text{H}_2\text{O}_2$  was added as oxidation agent in an alkaline medium during Experiments B, while oxidation was conducted in an acidic medium during Experiments C and subsequently the pH-value was increased to 9 for the precipitation.

These experiments were conducted with different additional amounts of 35% aqueous  $\text{H}_2\text{O}_2$  solution per liter of waste. The obtained results are summarized in Table 4. The percentage of residual arsenic is again related to the initial arsenic content (100%). The percentage of the separation degree of arsenic is complementary to the percentage of residual arsenic content and corresponds to the percentage of separated As, with respect to the initial As content.

TABLE 4

Reaction Conditions	As Initial (mg/l)	As Final (mg/l)	As Final %	As Separation %
EXPERIMENTS A (without oxidation)	6.9 6.9	2.8 3.3	40.6 47.8	59.4 52.2
EXPERIMENTS B (alkaline oxidation)				
H <sub>2</sub> O <sub>2</sub> , 35%:				
1 ml/l	6.9	1.4	20.3	79.7
3 ml/l	6.9	1.5	21.7	78.3
5 ml/l	6.9	1.5	21.7	78.3
7 ml/l	6.9	1.7	24.6	75.4
EXPERIMENTS C (acidic oxidation)				
H <sub>2</sub> O <sub>2</sub> , 35%				
1 ml/l	6.9	1.7	24.6	75.4
3 ml/l	6.9	1.8	26.1	73.9
5 ml/l	6.9	1.4	20.3	79.7
7 ml/l	6.9	1.7	24.6	75.4

The results show that oxidation of As(III) to As(V) increases the degree of separation considerably in all cases (from 50-60 to 74-80%), without showing any significant difference between an alkaline and an acidic oxidation. It is further apparent that the amounts of added  $H_2O_2$  have no relevant effect. Increasing the length of the reaction to more than 45 min. did not yield better results. The addition of the oxidation agent  $H_2O_2$  is preferred at a pH-value in the acidic range, since this secures a long enough reaction time and the oxidation agent cannot get into the exchanger.

#### Example 1 and Comparative Example 3

Example 1 refers to the separation of arsenic from waste material through precipitation of calcium magnesium arsenate of low solubility according to the steps A1 and A2 of the procedure according to the invention, while simultaneously using calcium magnesium compounds as precipitation.

Comparative Example 3 refers to the precipitation of arsenic with only the calcium compound. Milk of lime ( $Ca(OH)_2$ ) served as a calcium compound.  $Mg(OH)_2$  was used as a magnesium compound. The ratio of the amount of precipitation agents was  $Ca:Mg:AsO_4=3:3:1$ .

Precipitation occurred each time for 30 min. at a temperature of 25°C and a pH-value of >10.5. Effluents IV and VII (compare with Table 4) have been considered being of medium difficulty to be treated and waste VI as easy to be treated.

After the corresponding compounds have been added to the acidic crude waste water, the pH-value was raised to >10.5 and precipitation was carried out. Table 5 is a summary of the results obtained.

TABLE 5

	WASTE IV			WASTE VII			WASTE VI		
	As (mg/l) Initial	As (mg/l) Final	As Separation %	As (mg/l) Initial	As (mg/l) Final	As Separation %	As (mg/l) Initial	As (mg/l) Final	As Separation %
Comparative Example 3	28.5	19.9	30.2	14.0	8.0-9.0	35.7-42.9	6.9	3.0	56.5
Example 1	28.5	16.6	41.8 (+11.6)	14.0	5.4-6.0	57.1-61.4 (+14.2/25.7)	6.9	2.2	68.1 (+11.6)

The results in Table 5 give evidence that the procedure in Example 1 according to the invention, which used a combination of calcium and magnesium compounds, led to significantly better precipitation results compared to Comparative Example 3, which is performed under the same conditions, however using a calcium compound only. Those columns in which the degree of separation of arsenic is reflected also show in parenthesis the percentage of the additional separation degree that has been obtained in comparison to Comparative Example 3.

#### Examples 2 and 3 and Comparative Example 4

These experiments refer to the comparison of pure calcium arsenate precipitation (Comparative Example 4) for four different effluents with the procedure according to the invention. In this case the effluents were subject to precipitation using calcium and magnesium compounds without previous oxidation (Example 2) as well as after oxidation with  $H_2O_2$  (Example 3). The oxidation was carried out in an acidic pH-range.  $Ca(OH)_2$  was used as the calcium compound and  $Mg(OH)_2$  as the magnesium compound.

Effluents IV and VII were of medium difficulty to be treated; effluents VIII and IX were of high difficulty to be treated. The results obtained are summarized in Table 6.

TABLE 6

	WASTE VIII		As Separation %	WASTE VII		As Separation %	WASTE IX		As Separation %	WASTE IV		As Separation %
	As (mg/l) Initial	As (mg/l) Final		As (mg/l) Initial	As (mg/l) Final		As (mg/l) Initial	As (mg/l) Final		As (mg/l) Initial	As (mg/l) Final	
Comparative Example 4	10.6	8.9	16.0	14.0	8.0-9.0	35.7-42.9	22.4	17.6	21.4	28.5	20	29.8
Example 2	10.6	7.7	27.4 (+11.4)	14.0	5.4-6.0	57.1-61.4 (+14.2/25.7)	22.4	16.8	25.0 (+3.6)	28.5	16.6	41.8 (+12.0)
Example 3	10.6	5.2	50.9 (+34.9)	14.0	1.2-2.2	84.3-91.4 (+22.9/34.3)	22.4	13.8	38.4 (+17.0)	28.5	6.2	78.3 (+48.5)

The results in Table 6 reflect the significant improvement due to the procedure according to the invention of Examples 2 and 3 compared to the calcium arsenate precipitation (Comparative Example 4). This improvement was reflected for waste of medium treatment difficulty as well as in waste of high treatment difficulty. In the case of oxidation of arsenic in the waste to As(V) (Example 3), the separation result was again significantly better compared to Example 2.

Again the columns referring to the As-separation degree for Examples 2 and 3 reflect in parenthesis the additional degree of separation compared to Comparative Example 4.

#### Example 4

This example refers to the adsorptive separation of arsenic from waste material by means of setting the arsenic in contact with active carbon, hence the steps C1 and C2 of the procedure according to the invention. In these experiments industrial effluents with a high content of sulphate ions (effluents V) were used. By adding  $\text{Ca(OH)}_2$  at a pH-value of 3.0 the sulphate was precipitated as  $\text{CaSO}_4$  in 30 min. The precipitated mud was separated.

The pretreated waste obtained, which contained 33.5 mg As/l, was then treated with various amounts of active

carbon, after the pH-value had been adjusted by adding  $\text{Ca}(\text{OH})_2$ . The As-content was measured after every 30 min. The results obtained are reflected in Table 7.

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TABLE 7

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Amount Of Active Carbon (g/l)	pH at Adsorption	Initial As (mg/l)	Final As (mg/l)	Degree of As Separation %
0	3	33.5	33.5	0
5	>10.5	33.5	21.7	35.2
10	>10.5	33.5	13.5	59.7
15	>10.5	33.5	0.8	97.6

15

20

These results show that, in contrast to the initially mentioned bibliographic reference, the adsorptive separation of arsenic with active carbon is remarkably efficient because corresponding amounts of active carbon can yield exceptionally high degrees of arsenic separation (for example, 97.6% with 15 g of active carbon per liter).

25

The adsorption experiments conducted within this framework further showed that the efficiency of As-adsorption with active carbon practically does not depend on the medium's pH-value, which is in contact with

30

the active carbon. Furthermore the separation efficiency does not depend on whether or not the active carbon is separated.

Due to economical considerations the adsorption or separation of the active carbon is favorable at a pH-value of  $3 \pm 1$ . Most advantageous is the use of a regenerative active carbon solid filter bed with which the procedural steps C1 and C2 can be carried out simultaneously.

Since 1 kg of active carbon adsorbs 1.2 to 1.6 g of As, the corresponding measuring of the active carbon to be added to the solid bed filter can be done easily.

#### Example 5

This example refers to a preferred form of the invention according to the procedure, which separates residual arsenic contents by means of an ion exchanger, eventually after a previous separation of possible sulphate contents (compare to European patent application 86,108,876), and with or without a previous precipitation of arsenic in form of calcium magnesium arsenates. In this case a mixing-bed ion exchanger was used.

The amount of 160g (200ml) ion exchange resin was packed into a glass column (diameter of 2 cm), which was provided with a tap at one end. The height of packing was 80 cm. The sample was taken after a precisely defined

throughput at the column's outlet. The arsenic content was determined by atomic adsorption spectrometry as mentioned above.

Procedure conditions and analysis results:

Rate of flow:	1.0 l/h
Bed exchange:	6 fold
Initial pH:	11.5
Initial SO:	50 mg/l
Initial As:	14 mg/l
Conductivity (x)-initial:	2.3 mS/cm

After a 2 l throughput (= 8 l/l ion exchange resin):

pH-final:	6.5
SO <sub>4</sub> :	not traceable
Conductivity:	2.1 µS/cm
As:	2.5 µg/l

The above results show that a complete desalination has taken place. The ion exchanger exchanged not only the arsenic but all other caught ions. The low conductivity indicates a good quality of pure water.

The possibility of recycling the arsenic is very well provided if HCl is used as a regenerative agent for the two ion exchanger resins of the mixed bed. Hereby the anion exchanger is transformed into the Cl form and the cation exchanger is transformed into the H-form.

## Example 6

This example refers to the separation of residual arsenic from a pretreated waste similar to Example 5 during which, through pre-precipitation with milk of lime and subsequent precipitation with calcium aluminate sulfates, are separated to a large degree at a pH-value of 11.4 to 11.7. A highly basic, type I, anion exchanger in form Cl was used in those experiments.

In these experiments various amounts of resin (50, 75 or 200 g) were used, which were packed into a column with a diameter of 2 cm. The rate of flow and the therefore resulting bed exchange were varied. Regeneration occurred for 40 min. with 200 g HCl 100%/l ion exchanger resin in the form of a 5-8% solution, while the regenerative agent was led through the ion exchanger bed in the direction of the flow. The results obtained are summed up in Table 8.

TABLE 8

Resin Mass (g)	200	75	50	50
Rate of Flow (l/h)	4.5	1	1.1	0.67
Bed Exchange	28-fold	16-fold	18-fold	11-fold
SO <sub>4</sub> Initial (mg/l)	50	50	13	22
As Initial (mg/l)	15	15	14.7	15.5
X Initial (mg/l)	-	4.46	3.2	2.72
As Content (ppb) after 1 liter throughput	23.3	135	-	70.8
2 liters	-	-	10.1	69.2
3 liters	85.4	235	-	104.9
4 liters	-	-	8.7	84.4
5 liters	154.6	250	-	85.3
6 liters	-	-	10	101.0
7 liters	193.6	262	10.1	-
10 liters	233.7	-	-	-
X Final (mS/cm)	-	4.93	3.15	2.81

These results show that no eruption of arsenic occurred, even at a throughput of 7 l, which equals a load of 112 l/l ion exchange resin. This corresponds to capacity of close to 2.5 g As/l ion exchange resin. The best cleaning results were obtained at a low rate of flow.

A corresponding decrease in capacity occurs at sulfate concentrations which are too high, since the sulfate ion comes before the arsenic ion in the affinity sequence (compare to above). This requires the elimination of sulfate contents which are too high in a preliminary step, which can easily be done in the above mentioned procedure.

Further experiments determined the charge capacity of the highly basic anion exchanger used here.

#### CONDITIONS

pH:	11.5
SO <sub>4</sub> :	20 mg/l
Conductivity:	2.0 mS/cm
As-initially:	13.4 mg/l
Throughput:	1.2 l/h
Bed exchange:	8.5-fold
Interspersed volume:	35 l
As-final:	10 to 119 ppb
Conductivity (x)-final:	2.30 mS/cm
Amount of resin:	100 g



sulfide precipitation can be obtained and the arsenic can be regained. In this fashion recycling as well as other use, for example, depositing, is made possible.

With this invention a new concept of separating arsenic from waste has been provided. This process allows for a separation of this, to the environment, considerably harmful substance on a technical, industrial scale and under exceptionally economic conditions and in a chemically simple manner. Also important is that the process provides for recycling the separated arsenic into the production process.

Apart from arsenic other chemically similar anions such as chromate and phosphate can be separated from the waste.

The conception of the invention has particularly the following advantages:

- The procedure according to the invention can be applied to effluents difficult to be treated and strongly acidic waste, for example, waste from acidic polishing processes in the glass industry, which contain more than 10 mg As/l and for which a separation of arsenic through precipitation with Fe, Ca, etc. would not be efficient.

- Residual contents of As as low as  $< 1$  mg/l are possible by means of precipitation in the form of calcium magnesium arsenates ( $As < 2$  mg/l) and subsequent active carbon adsorption. In this case the active carbon is easily regenerated.
  
- The combination of arsenic precipitation in the form of calcium magnesium arsenate and/or adsorptive separation of arsenic with an ion exchanger yields residual amounts of arsenic of  $< 0.3$  mg As/l, which in suitable cases are in the low ppb-range.
  
- The arsenic can be precipitated easily and quantitatively sulfidic from the regenerative fluids of the ion exchanger regeneration.
  
- The regenerative solutions can be recirculated into a calcium precipitation step or can be "postsharpened."
  
- The concept of the procedure according to the invention can as well be applied to solutions containing sulfate; the main amount of sulfate can be separated by a preliminary precipitation of calcium at approximately pH-3, without coprecipitating arsenic,

which eventually, after washing the  $\text{CaSO}_4$  mud allows for a simple disposing on, for example, construction sites and household waste disposal sites. By means of a further precipitation in the form of calcium aluminate sulfates, residual  $\text{SO}_4$  amounts can be efficiently separated. As a preliminary step a considerable amount of the arsenic (estimated about 50 to 80%) can be selectively precipitated in form of calcium magnesium arsenate, which can be disposed of on special disposal sites.

- Tenside, which is present in waste material in significant amounts, does not interfere with either the preliminary sulfate precipitation or the precipitation of the calcium magnesium arsenates.

In view of the above description, it is likely that modifications and improvements to the invention will occur to those skilled in the art which are within the scope of the appended claims.

## WE CLAIM:

1. A process for the separation of arsenic from waste material, said process comprising the steps of:

(A1) precipitating arsenic in the form of low solubility calcium magnesium arsenates by adding at least one calcium compound and at least one magnesium compound to the waste material at a pH-value in the range of 2 to 12 during a precipitation span of 10 to 60 minutes;

(A2) separating the calcium magnesium arsenates;

(C1) adsorptively separating arsenic by putting the waste material in contact with active carbon at a pH-value in the range of 2 to 11; and

(C2) separating the charged active carbon by itself or along with precipitation products.

2. A process for the separation of arsenic from waste material, comprising the steps of:

(A1) precipitating arsenic in the form of low solubility calcium magnesium arsenates by adding at least one calcium compound and at least one magnesium compound to the waste material at a pH-value in the range of 2 to 12 during a precipitation span of 10 to 60 minutes;

(A2) separating the calcium magnesium arsenates;

(B1) putting the waste material in contact with an ion exchanger at a pH-value in the range of 2 to 12;

(C1) adsorptively separating arsenic by putting the waste in contact with active carbon at a pH-value in the range of 2 to 11; and

(C2) separating the charged active carbon by itself or along with precipitation products.

3. A process for the separation of arsenic from waste material, comprising the steps of:

(A1) precipitating arsenic in the form of low solubility

calcium magnesium arsenates by adding at least one calcium compound and at least one magnesium compound to the waste material at a pH-value in the range of 2 to 12 during a precipitation span of 10 to 60 minutes;

(A2) separating the calcium magnesium arsenates;

(B1) putting the waste material in contact with an ion exchanger at a pH-value in the range of 2 to 12;

(B2) regenerating the ion exchanger after reaching the charge limit;

(C1) adsorptively separating arsenic by putting the waste in contact with active carbon at a pH-value in the range of 2 to 11; and

(C2) separating the charged active carbon by itself or along with precipitation products.

4. A process for the separation of arsenic from waste material comprising the steps of:

(A1) precipitating arsenic in the form of low solubility calcium magnesium arsenates by adding at least one calcium compound and at least one magnesium compound to the waste material at a pH-value in the range of 2 to 12 during a precipitation span of 10 to 60 minutes

(B1) putting the waste material in contact with an ion exchanger, preferably a strongly basic anion exchanger, at a pH-value in the range of 2 to 12;

(C1) adsorptively separating arsenic by putting the waste in contact with active carbon at a pH-value in the range of 2 to 11; and

(C2) separating the charged active carbon by itself or along with precipitation products.

5. A process for the separation of arsenic from waste material comprising the steps of:

(A1) precipitating arsenic in the form of low solubility calcium magnesium arsenates by adding at least one calcium

compound and at least one magnesium compound to the waste material at a pH-value in the range of 2 to 12 during a precipitation span of 10 to 60 minutes;

(B1) putting the waste material in contact with an ion exchanger, preferably a strongly basic anion exchanger, at a pH-value in the range of 2 to 12;

(B2) regeneration of the ion exchanger after reaching the charge limit;

(C1) adsorptively separating arsenic by putting the waste in contact with active carbon at a pH-value in the range of 2 to 11; and

(C2) separating the charged active carbon by itself or along with precipitation products.

6. The process recited in claim 2, 3, 4 or 5, and comprising the further steps of oxidizing arsenic (III) in the waste material to  $\text{AsO}_4^{3-}$  by adding an oxidation agent selected from the group consisting of  $\text{CaO}_2$ ,  $\text{MgO}_2$  and  $\text{H}_2\text{O}_2$  and at a pH-value in the acidic range, to the waste material to be treated before step A1, B1 or C1 respectively.

7. The process recited in claim 3, and comprising the further step of:

separating sulfate ions from the waste material before step A1, B1 or C1 or after step A2, B2 or C2 respectively, by means of:

(I) precipitating  $\text{CaSO}_4$  by adding  $\text{Ca(OH)}_2$  to the waste, while the precipitation occurs:

before step A1 preferably at a pH-value of  $3 \pm 1$ ; or  
before step B1 or C1 respectively at pH-value in the range of  $3 \pm 1$  or 8.0 to 11.0;

(II) precipitating the low solubility calcium aluminate sulfates by adding reactive aluminum oxide and/or calcium aluminates to the waste material while regulating and maintaining the pH-value with  $\text{Ca(OH)}_2$  in the range of 11.2

to 11.8; and

(IV) separating the precipitated calcium aluminate sulfates.

8. The process recited in claim 7, and comprising the further step of (II) separating the precipitated  $\text{CaSO}_4$  and precipitated heavy metal hydroxide.

9. The process recited in claim 1, 2, 3, 4, 5, 6 or 7, and comprising the further step of adding one or more magnesium compounds in step A1 up to a pH-value in the alkaline range, so that magnesium hydroxide is precipitated.

10. The process recited in claim 1, 2, 3, 4, 5, 6, 7 or 9, wherein calcium hydrate is used as a calcium compound and/or magnesium hydroxide is used as a magnesium compound in step A1.

11. The process recited in claim 1, 2, 3, 4, 5, 6, 7 or 9, and comprising the further step of using mixtures of magnesium and calcium salts while adding  $\text{Ca}(\text{OH})_2$  in step A1.

12. The process recited in claim 1, 2, 3, 4, 5, 6, 7 or 9, wherein magnesium salts are used as a magnesium compound in step A1.

13. The process recited in claim 1, 2, 3, 4, 5, 6, 7, 9, 10, 11 or 12, wherein steps C1 and C2 are performed simultaneously by putting the waste material in contact with an active-carbon solid bed.

14. The process recited in claim 1, 2, 3, 4, 5, 6, 7, 9, 10, 11 or 12, wherein powdered active carbon is introduced into the waste material in step C1.

15. The process recited in claim 1, 2, 3, 4, 5, 6, 7, 9, 10,

11, 12, 13 or 14, and comprising the further step of regenerating by thermic means the charged active carbon from step C2, thereby gaining the arsenic.

16. The process recited in claim 1, 2, 3, 7, 8, 9, 10, 11, 12, 13, 14 or 15, and comprising the further step of washing the precipitation products or solid materials from steps A2 or C2 respectively with water, after setting the pH-value and recycling the water to the used crude waste water.

17. The process recited in claim 3, 5, 9, 10, 11, 12, 13, 14, 15 or 16, and comprising the further step of recycling the regenerative solutions from step B2 to the step of precipitation of arsenic in step A1 or the step of adsorptive separation of arsenic in step C1.

18. The process recited in claim 2, 3, 4, 5, 6, 7, 9, 10, 11, 12, 13, 14, 15, 16 or 17, wherein an anion exchanger in the form of chloride is used in step B1.

19. The process recited in claim 3, 5, 6, 9, 10, 11, 12, 13, 14, 15, 16, 17 or 18, wherein a mixed bed ion exchanger is used with a anion exchanger in the form of chloride and a cation exchanger in H-form in step B1 and the regeneration of the ion exchanger in step B2 is accomplished with hydrochloric acid as the regenerative agent.

20. The process recited in claim 7, 8, 9, 10, 11, 12, 13, 14, 15, 16 or 18, wherein the pH-value of  $3 \pm 1$  in step I is maintained.

21. The process recited in claim 6, 9, 10, 11, 12, 13, 14, 15 or 18, wherein the step of oxidating the arsenic (III) contained in the waste material before or in the precipitation reactor provides for the precipitation step to follow.

22. The process recited in claim 3, 5, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18 or 19, and comprising the further step of precipitating the arsenic, in the form of sulfides of arsenic, from the regenerative solutions resulting from step B2, separating those sulfides and recycling the obtained solutions in step A1, or in step C1, or using them again as regenerative solutions.

23. Apparatus for performing the process of separation of arsenic from waste material, said apparatus comprising the following elements, the sequence of which corresponds to the course of the reaction:

oxidation and precipitation reactor means for the precipitation of calcium magnesium arsenates;

an oxidation agent reservoir in communication with said oxidation and precipitation reactor means;

a calcium compound reservoir in selective communication with said oxidation and precipitation reactor means;

a magnesium compound reservoir in selective communication with said oxidation and precipitation reactor means;

pH-regulation means comprising a suitable reagent in a reservoir in selective communication with said oxidation and precipitation reactor means;

separation reactor means connected to said oxidation and precipitation reactor means for the separation of precipitated calcium magnesium arsenates from the residual water of the waste material; and

adsorption reactor means connected to the output of said separation reactor means for putting the waste material in contact with active carbon.

24. The apparatus recited in claim 23, and further comprising an ion exchanger coupled to the output of said separation reactor means.

25. The apparatus recited in claim 23 or 24, wherein said calcium compound reservoir and said magnesium compound reservoir are combined to one reservoir containing both compounds.

26. The apparatus recited in claim 23, 24 or 25, wherein said oxidation and precipitation reactor means and said separation reactor means are integrated to one reactor.

27. The apparatus recited in claim 23, 24, 25 or 26, wherein said adsorption reactor is an active-carbon solid bed reactor with a regeneration device which can yield the desorbed arsenic.

28. The apparatus recited in claim 24, 25, 26 or 27, wherein said ion exchanger is an anion exchanger or a mixed bed ion exchanger with a regeneration device.

29. The apparatus recited in claim 23, and further comprising:  
precipitation reactor means;  
a milk of lime reservoir in selective communication with said precipitation reactor;  
a calcium aluminate reservoir in selective communication with said precipitation reactor;  
second pH-regulation means comprising a suitable reagent in a reservoir in selective communication with said precipitation reactor;  
second separation reactor means connected to said precipitation reactor means for separating precipitated calcium sulfate or calcium aluminum sulfate, or both;  
said precipitation reactor means and said second separation reactor means being connected in said apparatus ahead of said oxidation and precipitation reactor means in the process, whereby the output of said precipitation reactor means and said second separation reactor means is coupled to the

input of said oxidation and precipitation reactor means.

30. The apparatus recited in claim 23, and further comprising:  
precipitation reactor means;

a milk of lime reservoir in selective communication with  
said precipitation reactor;

a calcium aluminate reservoir in selective communication  
with said precipitation reactor;

second pH-regulation means comprising a suitable reagent  
in a reservoir in selective communication with said  
precipitation reactor;

second separation reactor means connected to said  
precipitation reactor means for separating precipitated calcium  
sulfate or calcium aluminum sulfate, or both;

said precipitation reactor means and said second  
separation reactor means being connected in said apparatus  
between said oxidation and precipitation reactor means and said  
adsorption reactor means.

31. The apparatus recited in claim 24, and further comprising:  
precipitation reactor means;

a milk of lime reservoir in selective communication with  
said precipitation reactor;

a calcium aluminate reservoir in selective communication  
with said precipitation reactor;

second pH-regulation means comprising a suitable reagent  
in a reservoir in selective communication with said  
precipitation reactor;

second separation reactor means connected to said  
precipitation reactor means for separating precipitated calcium  
sulfate or calcium aluminum sulfate, or both;

said precipitation reactor means and said second  
separation reactor means being connected in said apparatus  
between said adsorption reactor and said ion exchanger.

32. The apparatus recited in claim 29, 30 or 31, wherein said separation reactor or said second separation reactor, or both, are sedimentation reactors or centrifuges.

Barrigar & Moss  
81 Metcalfe St., 7th Floor  
Ottawa, Ontario  
K1P 6K7

Agents for the Applicant

Agents for the Applicant  
Garcia, S. S. S.

2012472

Fig.1

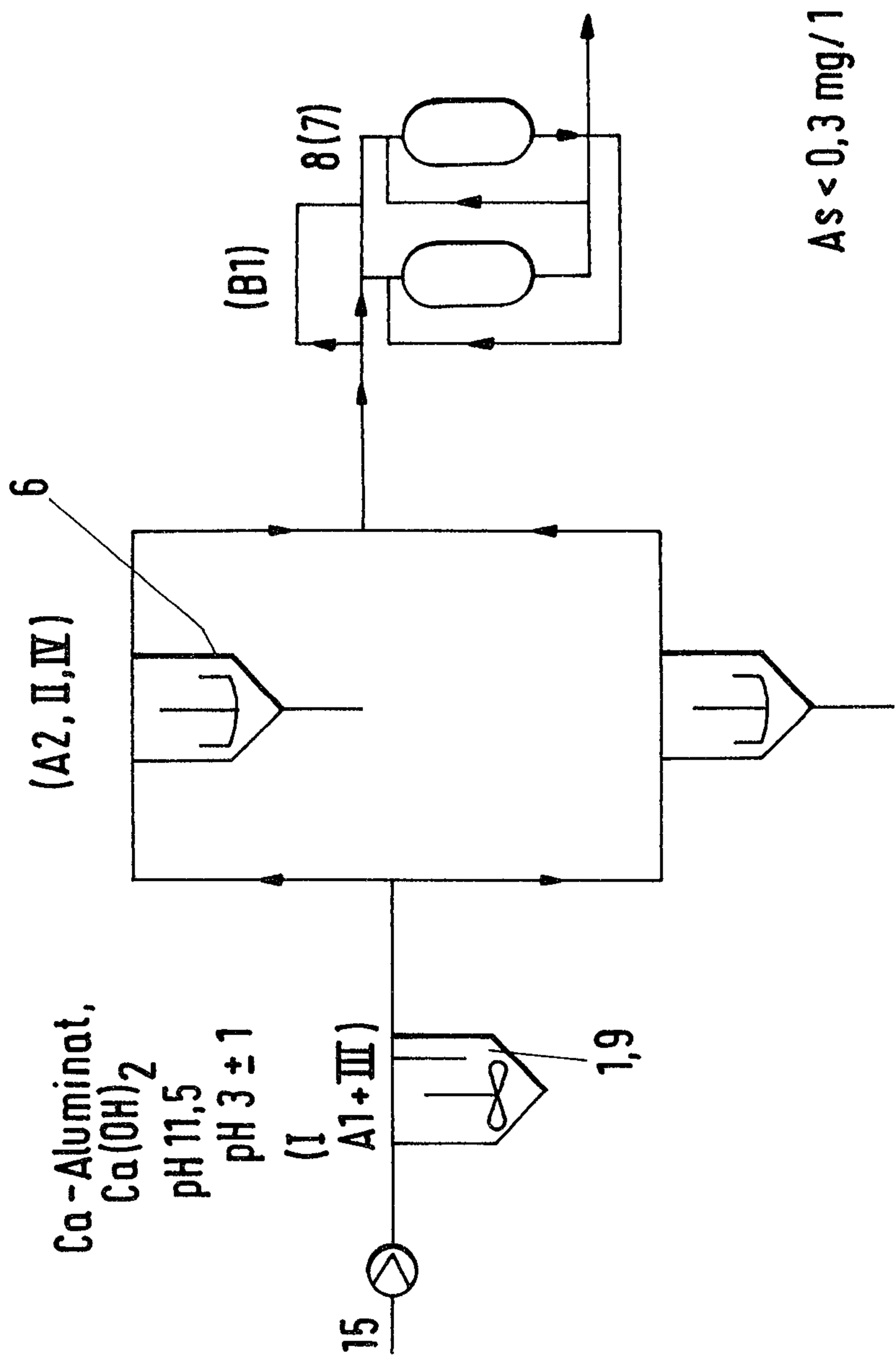
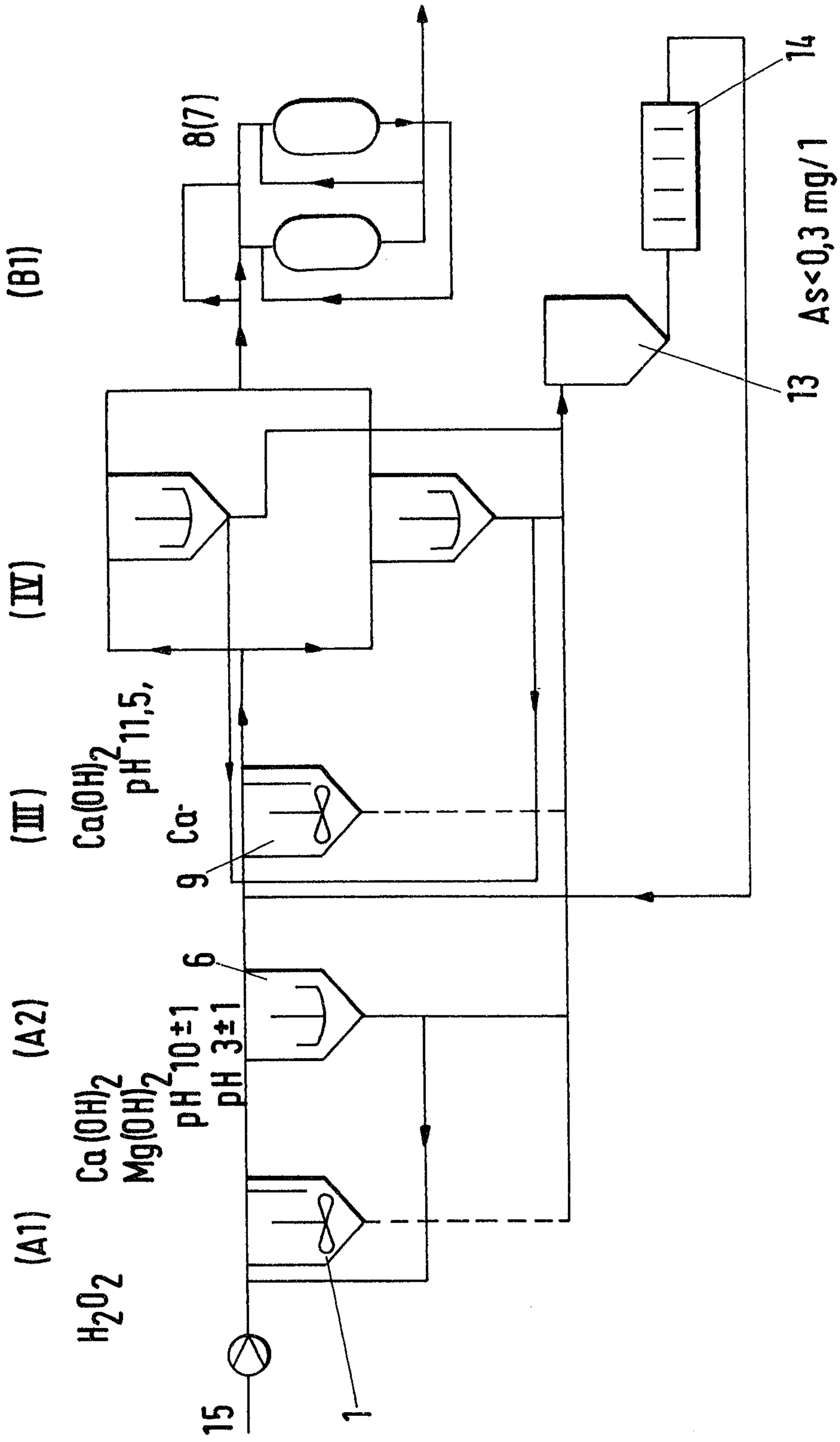


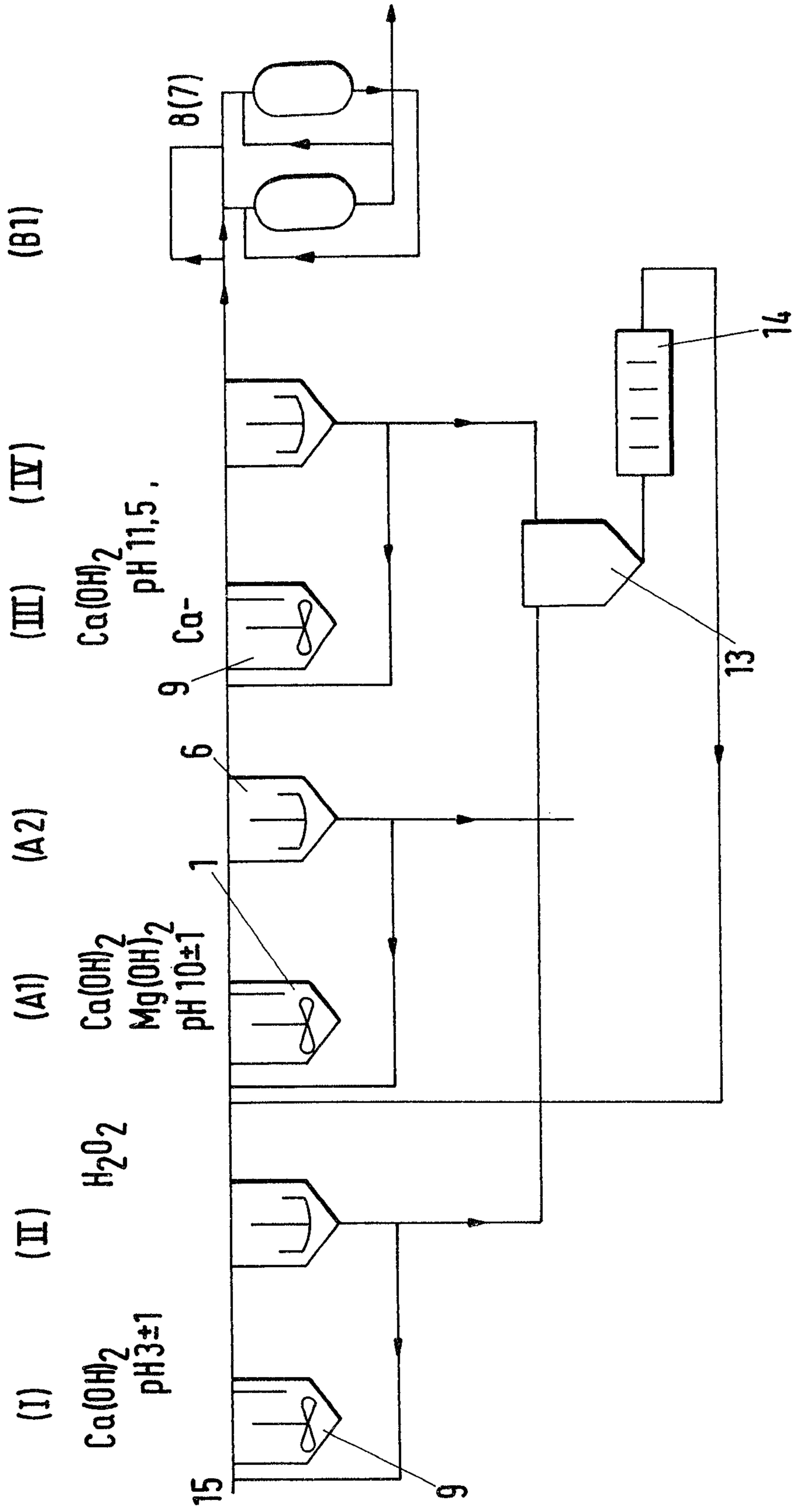
Fig.2



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Fig.3



As < 0,3 mg/l

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*Langen's Eye*  
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*Thomas & Berger  
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Fig. 4

